PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-236447
(43)Date of publication of application : 31.08.1999

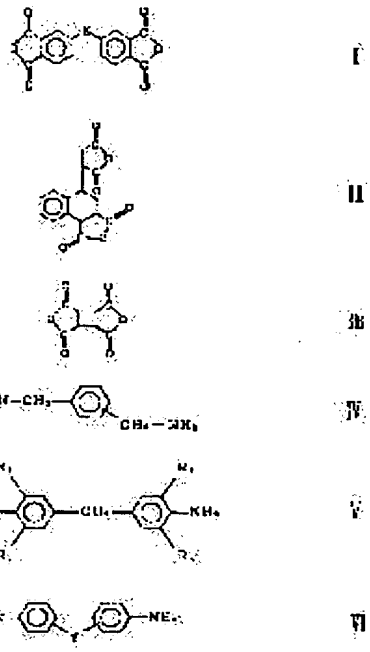
(51)Int.CI. C08G 73/10
H01F 27/24

(21)Application number : 10-041577
(22)Date of filing : 24.02.1998

(71)Applicant : MATSUSHITA ELECTRIC WORKS LTD
(72)Inventor : KIMURA TOSHIYUKI

(54) POLYIMIDE EVAPORATED POLYMERIZED FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain the subject film having improved flexibility, suppressing generation of cracking peeling, etc., when exposed to an external force such as mechanical processing, and having an excellent electrical insulating property.
SOLUTION: This polymerized film is obtained by subjecting (A) at least an acid anhydride of formulae I to III (X is nothing, CO, SO2, O, etc.) and (B) at least a diamine of formula IV, formula V (R1 to R4 are each CH3, C2H5 or C3H7) and formula VI (Y is O, CO, SO2, etc.), to an evaporated polymerization. Preferably, 3,3',4,4'-bisphenyltetracarboxylic acid anhydride is used as an acid anhydride and 2,2-bis[4-(4-aminophenoxy) pheny]propane is used as a diamine.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

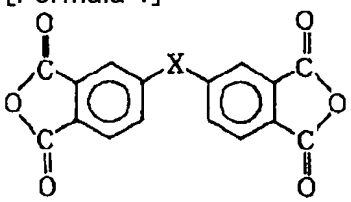
[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

CLAIMS

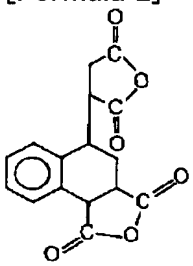
[Claim(s)]
[Claim 1] The polyimide vacuum evaporationo polymerization film characterized by being formed in at least one vacuum evaporationo polymerization among the diamines indicated to be at least one of the acid anhydrides shown by the following chemical formula (A) or (C) by the following chemical formula (D) or (F).
[Formula 1]



(A)

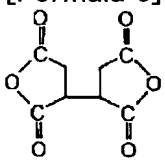
X=なし、CO, SO_2, O, $C(CF_3)_2$

[Formula 2]



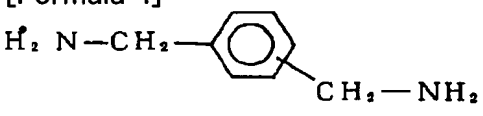
(B)

[Formula 3]



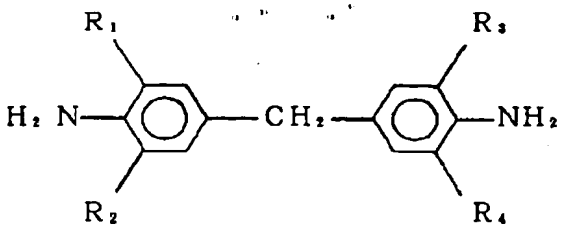
(C)

[Formula 4]



(D)

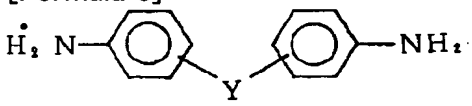
[Formula 5]



(E)

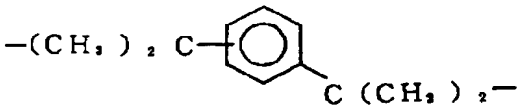
$R_1 \sim R_4 = CH_3$、C_2H_5、C_3H_7

[Formula 6]

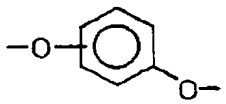


(F)

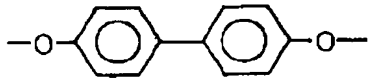
Y=O, CO, SO_2, CH_2,



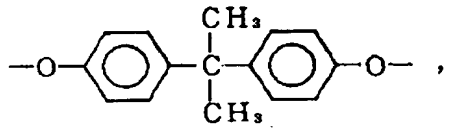
,



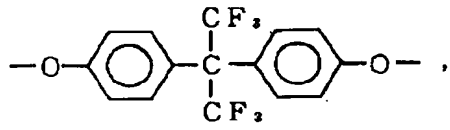
,



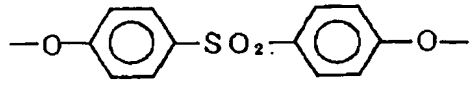
,



,

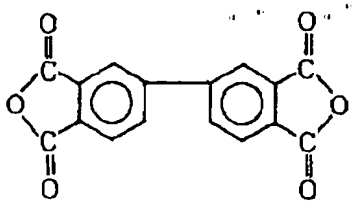


,

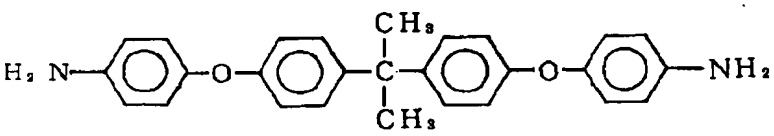


[Claim 2] an acid anhydride -- ****** -- the following -- a chemical formula -- (-- G --) -- being shown -- having -- three -- three -- ' -- four -- four -- ' -- - -- bisphenyl -- tetracarboxylic acid -- an anhydride -- using -- while -- a diamine -- ****** -- the following -- a chemical formula -- (-- H --) -- being shown -- having -- two -- two -- - -- a screw -- [-- four -- - (4-amino phenoxy) -- a phenyl --] -- a propane -- using --

[Formula 7]



(G)



(H)

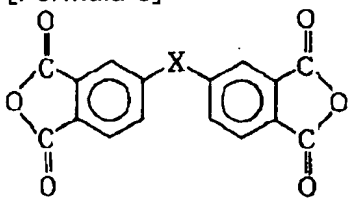
[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the polyimide vacuum evaporationo polymerization film formed in the vacuum evaporationo polymerization of an acid anhydride and a diamine.
[0002]
[Description of the Prior Art] There were some which are obtained by carrying out the vacuum evaporationo polymerization of PMDA (pyromellitic dianhydride)/the ODA (4 and 4'-diamino diphenyl ether) as a polyimide vacuum evaporationo polymerization film conventionally formed in the vacuum evaporationo polymerization of an acid anhydride and a diamine. and the thing for which such a polyimide vacuum evaporationo polymerization film is formed on a base material -- a base material -- electric insulation -- giving -- **** -- especially -- electromagnetism, such as an iron core of a relay, -- it was used for the pre-insulation of material etc.
[0003]
[Problem(s) to be Solved by the Invention] However, the above polyimide vacuum evaporationo polymerization films had the property in which it was hard and was weak, and after they formed the vacuum evaporationo polymerization film on the base material, when they performed machining etc. to this base material and external force was applied, the crack arose on the vacuum evaporationo polymerization film, or the ablation phenomenon of a vacuum evaporationo polymerization film occurred, and they had the problem that properties, such as the electric insulation of a base material, will fall.
[0004] this invention is made in view of the above-mentioned point, its flexibility improves, and it aims at offering the high polyimide vacuum evaporationo polymerization film of electric insulation with which generating of the crack at the time of external force, such as machining, acting, ablation, etc. was suppressed.
[0005]
[Means for Solving the Problem] The polyimide vacuum evaporationo polymerization film of this invention according to claim 1 is characterized by being formed in at least one vacuum evaporationo polymerization among the diamines indicated to be at least one of the acid anhydrides shown by the above-mentioned chemical formula (A) or (C) by the above-mentioned chemical formula (D) or (F).
[0006] this invention -- being according to claim 2 -- a polyimide -- vacuum evaporationo -- a polymerization -- a film -- a claim -- one -- composition -- in addition -- an acid anhydride -- ****** -- the above -- a chemical formula -- (-- G --) -- being shown -- having -- three -- three -- ' -- four -- four -- ' -- - -- bisphenyl -- tetracarboxylic acid -- an anhydride -- using -- while -- a diamine -- ****** -- the above -- a chemical formula -- (-- H --) -- being shown -- having -- two -- two
[0007]
[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained. The acid anhydride used by this invention is shown in the following chemical formula (A) or (C), and at least one is used for it.

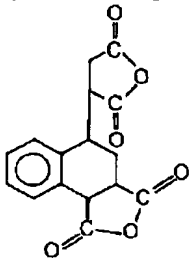
[0008]
[Formula 8]



(A)

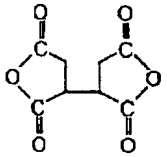
X=なし、CO, SO_2, O, $C(CF_3)_2$

[0009]
[Formula 9]



(B)

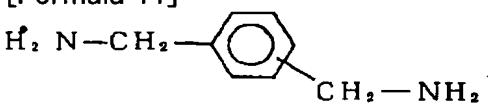
[0010]
[Formula 10]



(C)

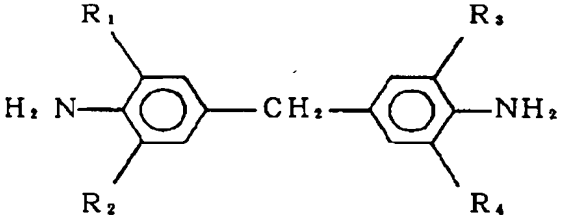
[0011] Moreover, the following chemical formula (D) or (F) shows the diamine used by this invention, and at least one is used for it.

[0012]
[Formula 11]



(D)

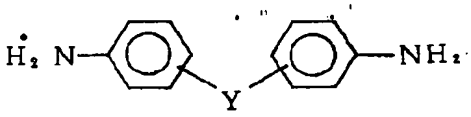
[0013]
[Formula 12]



(E)

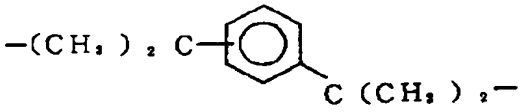
$R_1 \sim R_4 = CH_3$、C_2H_5、C_3H_7

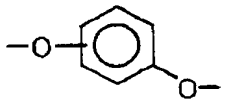
[0014]
[Formula 13]

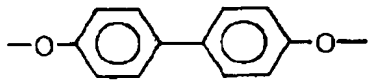


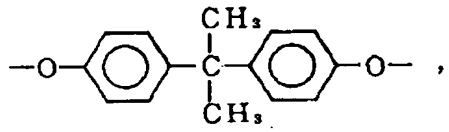
(F)

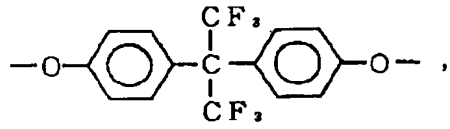
Y=O, CO, SO_2, CH_2,

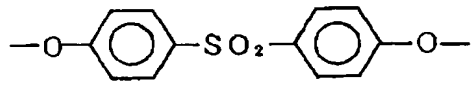








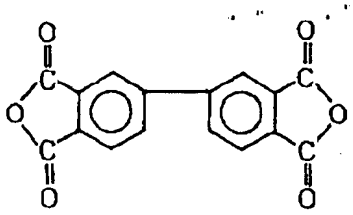




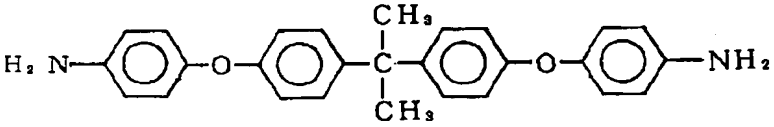
[0015] being such -- an acid anhydride -- and -- a diamine -- combination -- ****** -- for example -- the following -- a chemical formula -- (-- G --) -- being shown -- having -- three -- three -- ' -- four -- four -- ' -- - -- bisphenyl -- tetracarboxylic acid -- an anhydride (PMDA) -- the following -- a chemical formula -- (-- H --) -- being shown -- having -- two -- two -- - -- a screw -- [-- four -- - (4-amino phenoxy) -- a phenyl --]

[0016]

[Formula 14]



(G)



(H)

[0017] In case the polyimide vacuum evaporationo polymerization film of this invention is formed on a base material, a vacuum evaporationo polymerizer as shown in drawing 1 can be used. The heater 2 for vacuum evaporationo tubs is prepared in the surroundings of the vacuum evaporationo tub 1 so that the enclosure of the vacuum evaporationo tub 1 may be carried out, and it enables it to have heated the vacuum evaporationo space 3 formed in the vacuum evaporationo tub 1 in this vacuum evaporationo polymerizer. Moreover, the vacuum pump 7 is connected to the vacuum evaporationo tub 1, and it enables it to have decompressed the inside of the vacuum evaporationo space 3 with the vacuum pump 7.

[0018] Moreover, from the outside of the vacuum evaporationo tub 1, the two conductance sections 11a and 11b insert in in the vacuum evaporationo space 3, and are prepared in the vacuum evaporationo tub 1. These conductance sections 11a and 11b are formed in the shape of a closed-end cylinder, arrange a pars basilaris ossis occipitalis in the vacuum evaporationo space 3, and arrange opening out of the vacuum evaporationo tub 1. moreover, two or more passage [portion / which is arranged in the vacuum evaporationo space 3 of the conductance sections 11a and 11b] -- Holes 10a and 10b are drilled The raw material generating tubes 8a and 8b are connected to opening of vacuum evaporationo tub 1 outside of each conductance sections 11a and 11b, respectively, the heaters 9a and 9b for raw material generating tubes are formed in the surroundings of these raw material generating tubes 8a and 8b so that the enclosure of the raw material generating tubes 8a and 8b may be carried out, and it enables it to have heated the raw material generating tubes 8a and 8b.

[0019] Moreover, while forming superficies reticulated in the vacuum evaporationo space 3, the rotation barrel 4 formed in tubed [which both ends closed] is arranged. The axis of rotation 5 inserted in in the vacuum evaporationo space 3 is connected to this rotation barrel 4 from the outside of the vacuum evaporationo tub 1, a motor 6 is connected to the edge of vacuum evaporationo tub 1 outside of the axis of rotation 5, axial rotation of the axis of rotation 5 is carried out by the motor 6, and it enables it to have rotated the rotation barrel 4.

[0020] How to form a polyimide vacuum evaporationo polymerization film in a base material U using such a vacuum evaporationo polymerizer is explained. While supplying the acid anhydride S which consists of at least one thing in the acid anhydride first shown in raw material generating tube 8a which is one side beforehand by the above (A) or (C), the diamine T which consists of at least one thing in the diamine shown in raw material generating tube 8b of another side by the above (D) or (F) is supplied, and a base material U is supplied in the rotation barrel 4. And a vacuum pump 7 is operated and the inside of the vacuum evaporationo space 3 is decompressed to the suitable pressure for vacuum evaporationo polymerization reaction. The pressure in the vacuum evaporationo space 3 is set to 1x10-1 - 5x10-5Torr here, and advancing vacuum evaporationo polymerization reaction under this flow and pressure requirement sets to 1x10-2 - 1x10-3Torr desirable still more preferably. Moreover, while operating a motor 6 and rotating the rotation barrel 4, the base material U in the vacuum evaporationo space 3 is heated to the suitable reaction temperature for vacuum evaporationo polymerization reaction at the heater 2 for vacuum evaporationo tubs. It is desirable to heat a base material U at 180-250 degrees C

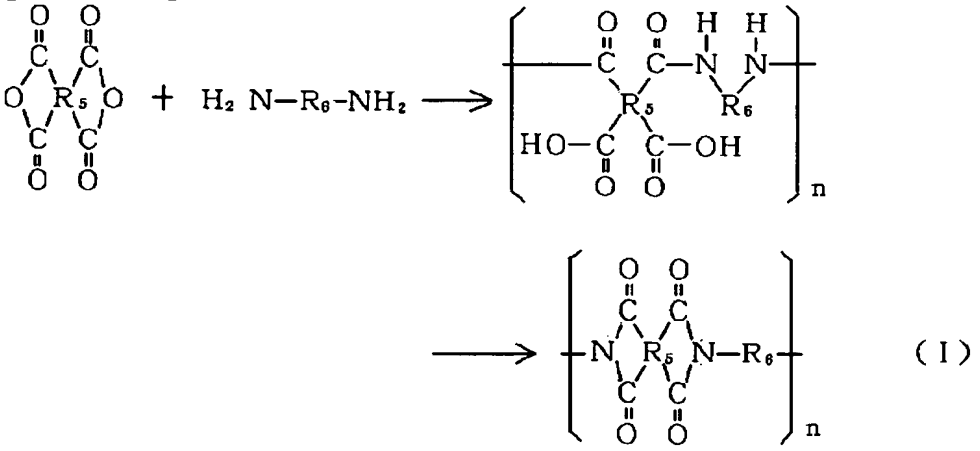
here, and to advance vacuum evaporationo polymerization reaction under these temperature conditions.

[0021] Next, each raw material generating tubes 8a and 8b are heated at the heaters 9a and 9b for raw material generating tubes, and the acid anhydride S and Diamine T in each raw material generating tube 8a and 8b are evaporated. In order to evaporate an acid anhydride S at this time, making an acid anhydride S heat to 180-300 degrees C considers as 220-260 degrees C desirable still more preferably, and in order to evaporate [and] Diamine T, it may be 200-240 degrees C to make Diamine T heat to 180-280 degrees C desirable still more preferably. thus, the acid anhydride S which evaporated, and Diamine T are introduced in the vacuum evaporationo tub 1 through each conductance sections 11a and 11b -- having -- passage of the conductance sections 11a and 11b -- it is guided in the vacuum evaporationo space 3 through Holes 10a and 10b, and reaches to a base material U The acid anhydride S and Diamine T which reached the base material U form a polyimide vacuum evaporationo polymerization film by vacuum evaporationo polymerization reaction on a base material U.

[0022] As shown in the following reaction formula (I), after an acid anhydride and a diamine react first and a polyamic-acid film is formed, formation of the polyimide vacuum evaporationo polymerization film by vacuum evaporationo polymerization reaction is performed here, when the dehydration ring closure reaction of a polyamic acid advances.

[0023]

[Formula 15]



(I)

[0024] It is R5 in a formula, and R6 here. The portion shown is arbitrarily chosen so that it may correspond to the acid anhydride and diamine which are shown by the formula (A) or (F), and n is the natural number. thus, the thing which neither a crack nor ablation can produce easily even if the polyimide vacuum evaporationo polymerization film of this invention formed can form thickness uniformly, and flexibility is high, and it performs machining etc. to the base material in which the polyimide vacuum evaporationo polymerization film was formed and applies external force -- it is -- electromagnetism -- in case it applies to the base material used for material, the electric insulation and surface-protection nature can be improved

[0025]

[Example] Hereafter, this invention is explained in full detail according to an example.

(An example 1 or 9) as a base material -- electromagnetism, as press working of sheet metal is performed to soft iron and it is shown in drawing 2 To the ends of a base (width-of-face d1 =13mm, depth d4 =3mm, and thickness d5 =1mm) 13 The iron core 12 of the configuration where the piece sections (height d6 =3mm and thickness d3 =1mm) 14 and 14 were set up, and the size between the piece section 14 and 14 was set to d2 =11mm was formed, and copper plating and nickel plating were performed to this front face.

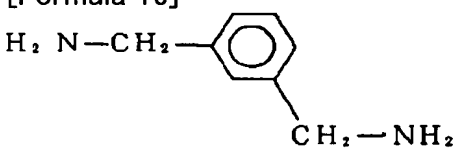
[0026] About each example, the polyimide vacuum evaporationo polymerization film was formed in the above-mentioned iron core 12 using the acid anhydride and diamine which are shown in Table 1. When forming a polyimide vacuum evaporationo polymerization film, the acid anhydride was evaporated at 280 degrees C, it evaporated the diamine at 260 degrees C, it introduced to

the vacuum evaporationo tub, using an acid anhydride and a diamine 20g each, and the polyimide vacuum evaporationo polymerization film of thickness shown in Table 1 was formed on the iron core 12 within the vacuum evaporationo tub on condition that reaction temperature [of 230 degrees C], and reaction pressure 2x10-2Torr.

[0027] The acid anhydride in Table 1 (G), (B), and (C) are acid anhydrides shown by the above-mentioned chemical formula (G), (B), and (C), respectively, and the diamine a diamine (H) is indicated to be with the above-mentioned chemical formula (H), a diamine (J), and (K) are diamines shown by the following chemical formula (J) and (K) here, respectively.

[0028]

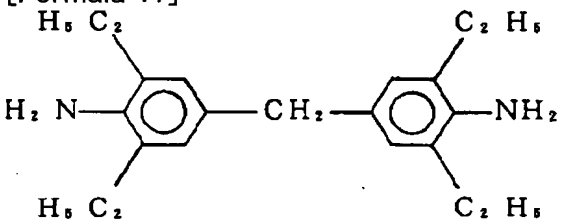
[Formula 16]



(J)

[0029]

[Formula 17]



(K)

[0030] (Example 1 of comparison) While using the acid anhydride shown with the above-mentioned chemical formula (G) as an acid anhydride, except having used ODA (4 and 4'-diamino diphenyl ether) as a diamine, it carried out like the example 1 and the polyimide vacuum evaporationo polymerization film of 10 micrometers of thickness was formed in the iron core 12.

(Initial withstand-voltage evaluation) After coiling about the phi0.042mm lead wire which gave urethane covering around the iron core 12 in which the polyimide vacuum evaporationo polymerization film of each example and the example of comparison was formed, 20 times, while removing covering of the end of lead wire to it, a part of polyimide vacuum evaporationo polymerization film of an iron core 12 was removed to it, and the metal side was exposed to it. It prepared such 30 samples at a time about each example and the example of comparison, the probe was applied to the metal exposed surface of an iron core 12, and the metal exposed surface of lead wire, respectively, and voltage was impressed by the slow rise with the dielectric-breakdown-test vessel (the product made from the Kikusui electron, lot number "TOS8650"), and when a leakage current was 10mA, it evaluated as what dielectric breakdown produced.

(Withstand-voltage evaluation after machining) The iron core 12 in which the polyimide vacuum evaporationo polymerization film formed in each example and the example of comparison was formed Pouring of a LCP resin to metal mold 15 it is shown in drawing 3 (a) -- as -- ends -- a fixture 16 -- fixing -- near the edge of the base 13 of an iron core 12 -- fabrication -- while attaching metal mold 15 -- this fabrication -- As it was made to harden and was shown in drawing 3 (b), the flange section 17 which consists of a LCP resin moldings was formed near the edge of a base 12. Furthermore, applying the tension of 4g for the phi0.042mm lead wire 19 which gave urethane covering to the portion pinched by the flange section 15 of the base 13 of this iron core 12 at this lead wire 19, as shown in drawing 3 (c), 15000 turn volume times were carried out with the winding machine, and the coil 18 was formed. It prepared such 30 samples at a time about each example and the example of comparison, and the withstand voltage was evaluated like the case of initial withstand-voltage evaluation about this coil 18.

(Surge voltage-proof evaluation) Using the iron core 12 of each example and the example of comparison, the coil 18 was formed like the time of the withstand-voltage evaluation after

machining, and it finished setting up a relay using this coil 18. It prepared such 30 samples at a time about each example and the example of comparison, and between this relay contact and the end-winding child, peak value was raised to every 250V from 1500V, surge voltage was repeatedly impressed by the standard impulse voltage wave of 1.2x50microsec., and the threshold value which dielectric breakdown produces was measured.

[0031] The above result is shown in Table 1.

[0032]

[Table 1]

			実施例									比較例
			1	2	3	4	5	6	7	8	9	1
薬着複合膜	酸無水物		(G)	(G)	(G)	(B)	(B)	(B)	(C)	(C)	(C)	(G)
	ジアミン		(H)	(J)	(K)	(H)	(J)	(K)	(H)	(J)	(K)	ODA
	膜厚 (μm)		8	8	8	8	8	8	8	8	8	10
評価試験	初期耐電圧 (V)	平均値	2210	2110	2140	2240	2170	2180	2040	1980	2140	2000
		最大値	2550	2440	2410	2500	2400	2410	2410	2320	2410	2430
		最小値	1950	1900	1880	1980	1880	1930	1780	1880	1880	1850
	機械加工後の耐電圧 (V)	平均値	2250	2150	2190	2220	2180	2190	2010	2090	2190	1750
		最大値	2650	2530	2530	2580	2500	2590	2380	2430	2530	2200
		最小値	1900	1790	1850	1950	1820	1960	1870	1850	1980	1200
	耐サージ電圧 (V)	平均値	2130	1980	2070	2110	2020	2070	2000	1940	1930	1900
		最大値	2250	2250	2250	2250	2250	2250	2250	2250	2250	2000
		最小値	2000	1750	2000	2000	1750	2000	1750	1750	1750	1750

[0033] Table 1 shows -- as -- the example 1 of comparison -- an initial withstand voltage -- comparing -- the withstand voltage after machining -- falling -- moreover, surge voltage-proof -- an example 1 or the thing of 9 -- low -- fixation in the fixture 16 of an iron core 12, and fabrication -- attachment of metal mold 15 and lead wire 19 -- winding -- a time -- carrying out -- etc. -- by the external force by machining, a crack and exfoliation of a polyimide vacuum evaporationo polymerization film arise, and the electric insulation of an iron core 12 falls At an example 1 or the thing of 9, there was almost no difference of an initial withstand voltage and the withstand voltage after machining, and after surge voltage-proof was also higher than the thing of the example 1 of comparison and external force was applied by the high flexibility of the polyimide vacuum evaporationo polymerization film of this invention with machining to it, the crack of a polyimide vacuum evaporationo polymerization film and generating of exfoliation were suppressed, and it has checked that the electric insulation of an iron core 12 was maintainable.

[0034]

[Effect of the Invention] As mentioned above the polyimide vacuum evaporationo polymerization film of this invention Since it is formed in at least one vacuum evaporationo polymerization among the diamines indicated to be at least one of the acid anhydrides shown by the above-mentioned chemical formula (A) or (C) by the above-mentioned chemical formula (D) or (F), the crack of the polyimide vacuum evaporationo polymerization film at the time of performing machining etc. to the base material in which ****** was high and formed this polyimide vacuum evaporationo polymerization film, and applying external force, and generating of exfoliation -- it can suppress -- as a base material -- electromagnetism -- the electric insulation of the base material when using material can be improved

---

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12) **公開特許公報（Ａ）**　(11)特許出願公開番号

特開平11－236447

(43)公開日　平成11年(1999) 8月31日

(51)Int.Cl.[6]	識別記号	ＦＩ	
Ｃ０８Ｇ　73/10		Ｃ０８Ｇ　73/10	
Ｈ０１Ｆ　27/24		Ｈ０１Ｆ　27/24	Ｑ

審査請求　未請求　請求項の数２　ＯＬ　（全 9 頁）

(21)出願番号　特願平10－41577

(22)出願日　平成10年(1998) 2月24日

(71)出願人　000005832
松下電工株式会社
大阪府門真市大字門真1048番地

(72)発明者　木村　俊之
大阪府門真市大字門真1048番地松下電工株式会社内

(74)代理人　弁理士　西川　惠清　（外１名）

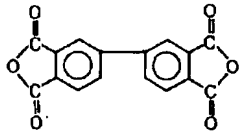
(54)【発明の名称】　ポリイミド蒸着重合膜

(57)【要約】

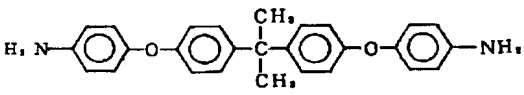
【課題】　可撓性が向上され、機械加工等の外力が作用された際のひび割れ、剥離等の発生が抑制された、電気絶縁性の高いポリイミド蒸着重合膜を提供する。　＊

＊【解決手段】　下記化学式（Ｇ）等で示される酸無水物と、下記化学式（Ｈ）等で示されるジアミンとの蒸着重合にて形成される。

【化１】



(G)



(H)

1

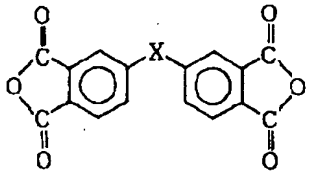
【特許請求の範囲】

【請求項１】　下記化学式（Ａ）乃至（Ｃ）で示される酸無水物のうち少なくとも一つと、下記化学式（Ｄ）乃至（Ｆ）で示されるジアミンのうち少なくとも一つとの＊

2

＊蒸着重合にて形成されることを特徴とするポリイミド蒸着重合膜。

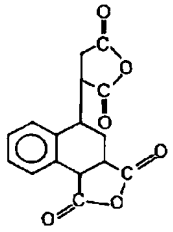
【化１】



(A)

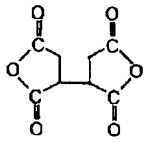
X＝なし、CO, SO_2, O, $C(CF_3)_2$

【化２】



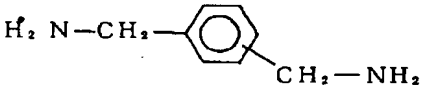
(B)

【化３】



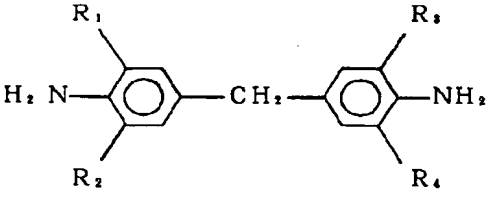
(C)

【化４】



(D)

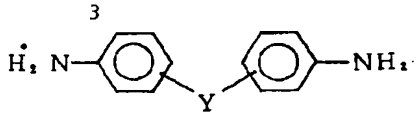
【化５】



(E)

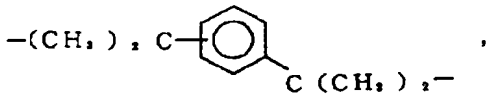
R_1～R_4＝CH_3、C_2H_5、C_3H_7

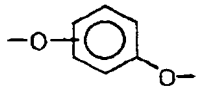
【化６】

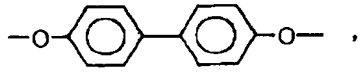


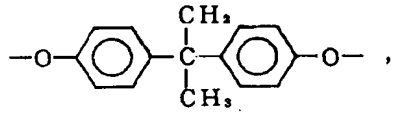
(F)

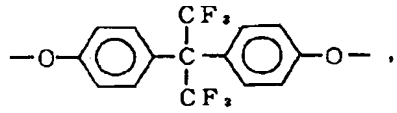
Y＝O，CO，SO_2，CH_2，

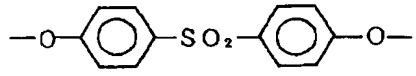






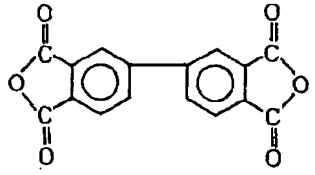




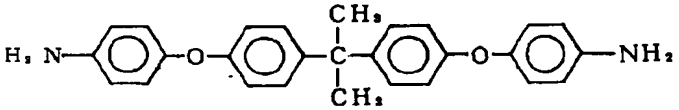


【請求項２】酸無水物として下記化学式（Ｇ）で示される、３，３’，４，４’－ビスフェニルテトラカルボン酸無水物を用いると共に、ジアミンとして下記化学式（Ｈ）で示される２，２－ビス［４－（４－アミノフェ＊ノキシ）フェニル］プロパンを用いて形成されたことを特徴とする請求項１に記載のポリイミド蒸着重合膜。

【化７】



(G)



(H)

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、酸無水物とジアミンとの蒸着重合にて形成されるポリイミド蒸着重合膜に

5

関するものである。

【０００２】

【従来の技術】従来酸無水物とジアミンとの蒸着重合にて形成されるポリイミド蒸着重合膜としては、ＰＭＤＡ（無水ピロメリット酸）／ＯＤＡ（４，４’－ジアミノジフェニルエーテル）を蒸着重合して得られるものがあった。そしてこのようなポリイミド蒸着重合膜を基材上に形成することによって、基材に電気絶縁性を付与していたものであり、特にリレーの鉄芯等の電磁材料の絶縁被覆等に用いられていた。

【０００３】

【発明が解決しようとする課題】しかし上記のようなポリイミド蒸着重合膜は硬く脆いという性質があり、基材上に蒸着重合膜を形成した後この基材に機械加工等を行って外力を加えると、蒸着重合膜にひび割れが生じたり、蒸着重合膜の剥離現象が発生したりして、基材の電気絶縁性等の特性が低下してしまうという問題があった。

【０００４】本発明は上記の点に鑑みてなされたものであり、可撓性が向上され、機械加工等の外力が作用された際のひび割れ、剥離等の発生が抑制された、電気絶縁性の高いポリイミド蒸着重合膜を提供することを目的と＊

6

＊するものである。

【０００５】

【課題を解決するための手段】本発明の請求項１に記載のポリイミド蒸着重合膜は、上記化学式（Ａ）乃至（Ｃ）で示される酸無水物のうち少なくとも一つと、上記化学式（Ｄ）乃至（Ｆ）で示されるジアミンのうち少なくとも一つとの蒸着重合にて形成されることを特徴とするものである。

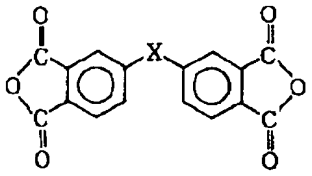
【０００６】本発明の請求項２に記載のポリイミド蒸着重合膜は、請求項１の構成に加えて、酸無水物として上記化学式（Ｇ）で示される、３，３’，４，４’－ビスフェニルテトラカルボン酸無水物を用いると共に、ジアミンとして上記化学式（Ｈ）で示される２，２－ビス［４－（４－アミノフェノキシ）フェニル］プロパンを用いて形成されたことを特徴とするものである。

【０００７】

【発明の実施の形態】以下、本発明の実施の形態を説明する。本発明で用いる酸無水物は、下記の化学式（Ａ）乃至（Ｃ）に示すものであり、このうち少なくとも一つを用いるものである。

【０００８】

【化８】

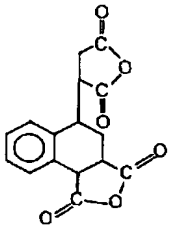


（Ａ）

Ｘ＝なし、ＣＯ，SO_2，Ｏ，$C(CF_3)_2$

【０００９】

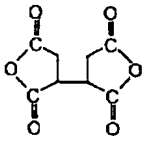
※30※【化９】



（Ｂ）

【００１０】

★ ★【化１０】



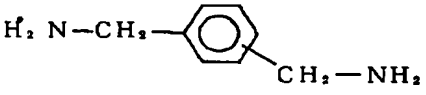
（Ｃ）

【００１１】また本発明で用いるジアミンは、下記化学式（Ｄ）乃至（Ｆ）で示すものであり、このうち少なくとも一つを用いるものである。

☆

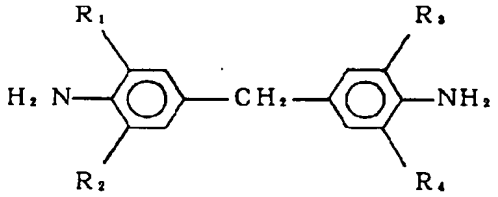
☆【００１２】

【化１１】



（Ｄ）

【００１３】　＊　＊【化１２】



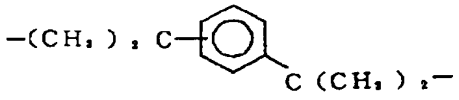
(E)

$R_1 \sim R_4 = CH_3$、C_2H_5、C_3H_7

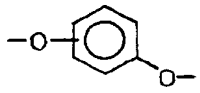
【００１４】　※　※【化１３】

(F)

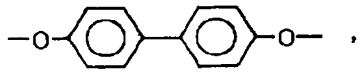
Y＝O，CO，SO_2，CH_2，



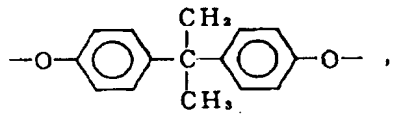
，



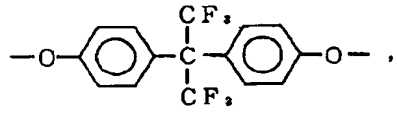
，



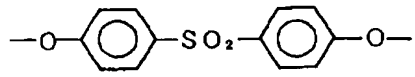
，



，



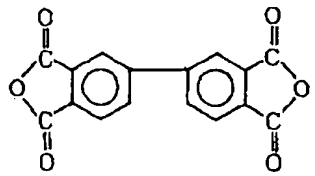
，



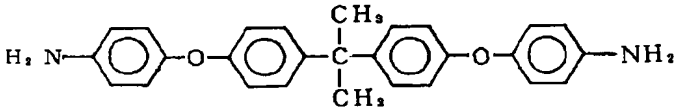
【００１５】このような酸無水物及びジアミンの組合せとしては、例えば下記化学式（Ｇ）で示される、３，３’，４，４’－ビスフェニルテトラカルボン酸無水物（ＰＭＤＡ）と、下記化学式（Ｈ）で示される２，２－ビス［４－（４－アミノフェノキシ）フェニル］プロパン（ＢＡＰＢ）との組合せを挙げることができる。

【００１６】

【化１４】



（G）



（H）

【００１７】本発明のポリイミド蒸着重合膜を基材上に形成する際には、例えば図１に示すような蒸着重合装置を用いることができる。この蒸着重合装置では、蒸着槽１の廻りに蒸着槽用ヒーター２を、蒸着槽１を外囲するように設けてあり、蒸着槽１内に形成される蒸着空間３を加熱できるようにしてある。また蒸着槽１には真空ポンプ７が接続してあり、真空ポンプ７にて蒸着空間３内を減圧できるようにしてある。

【００１８】また蒸着槽１には二つのコンダクタンス部１１ａ、１１ｂが蒸着槽１外から蒸着空間３内に挿通して設けてある。このコンダクタンス部１１ａ、１１ｂは有底円筒状に形成してあり、底部を蒸着空間３内に配置し、開口部を蒸着槽１外に配置してある。またコンダクタンス部１１ａ、１１ｂの蒸着空間３内に配置される部分には複数の通過孔１０ａ、１０ｂが穿設してある。各コンダクタンス部１１ａ、１１ｂの蒸着槽１外側の開口にはそれぞれ原料蒸発管８ａ、８ｂを接続するものであり、この原料蒸発管８ａ、８ｂの廻りには原料蒸発管用ヒーター９ａ、９ｂを原料蒸発管８ａ、８ｂを外囲するように設けて、原料蒸発管８ａ、８ｂを加熱できるようにしてある。

【００１９】また蒸着空間３内には外面を網状に形成すると共に両端部が閉じた筒状に形成した回転バレル４が配置してある。この回転バレル４には蒸着槽１外から蒸着空間３内に挿通する回転軸５が接続してあり、回転軸５の蒸着槽１外側の端部にはモーター６を接続して回転軸５をモーター６にて軸回転させて回転バレル４を回転できるようにしてある。

【００２０】このような蒸着重合装置を用いて基材Ｕにポリイミド蒸着重合膜を形成する方法を説明する。まずあらかじめ一方の原料蒸発管８ａに上記（Ａ）乃至（Ｃ）で示される酸無水物のうちの少なくとも一つのものから成る酸無水物Ｓを投入すると共に、他方の原料蒸発管８ｂに上記（Ｄ）乃至（Ｆ）で示されるジアミンのうちの少なくとも一つのものから成るジアミンＴを投入し、また回転バレル４内に基材Ｕを投入する。そして真空ポンプ７を作動させて蒸着空間３内を蒸着重合反応に好適な圧力まで減圧する。ここで蒸着空間３内の圧力は1×10^{-1}～5×10^{-5}Ｔｏｒｒとし、この圧力条件下で蒸着重合反応を進行させることが好ましく、更に好ましくは、1×10^{-2}～1×10^{-3}Ｔｏｒｒとするものである。またモーター６を作動させて回転バレル４を回転させると共に蒸着槽用ヒーター２にて蒸着空間３内の基材Ｕを、蒸着重合反応に好適な反応温度まで加熱する。ここで基材Ｕは１８０～２５０℃に加熱し、この温度条件下で蒸着重合反応を進行させることが好ましい。

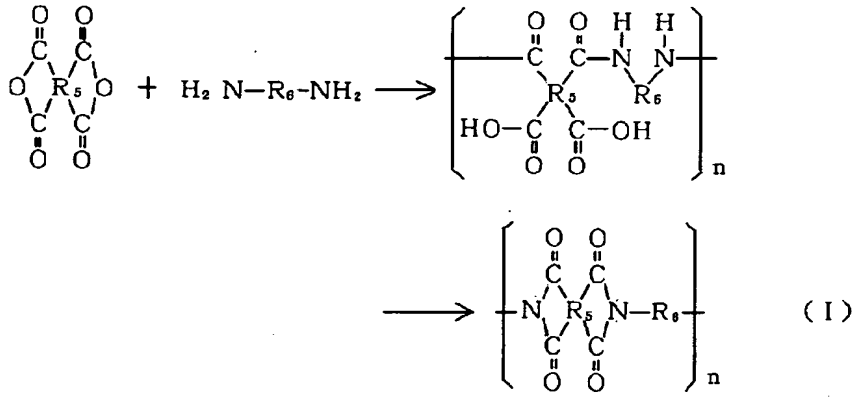
【００２１】次に各原料蒸発管８ａ、８ｂを原料蒸発管用ヒーター９ａ、９ｂにて加熱して各原料蒸発管８ａ、８ｂ内の酸無水物Ｓ及びジアミンＴを蒸発させる。このとき酸無水物Ｓを蒸発させるためには酸無水物Ｓを１８０～３００℃まで加熱させることが好ましく、更に好ましくは２２０～２６０℃とするものであり、またジアミンＴを蒸発させるためにはジアミンＴを１８０～２８０℃まで加熱させることが好ましく、更に好ましくは２００～２４０℃とするものである。このようにして蒸発された酸無水物Ｓ及びジアミンＴは、各コンダクタンス部１１ａ、１１ｂを通じて蒸着槽１内に導入され、コンダクタンス部１１ａ、１１ｂの通過孔１０ａ、１０ｂを通じて蒸着空間３内に誘導されて、基材Ｕまで達する。基材Ｕに達した酸無水物Ｓ及びジアミンＴは基材Ｕ上で蒸着重合反応により、ポリイミド蒸着重合膜を形成する。

【００２２】ここで蒸着重合反応によるポリイミド蒸着重合膜の形成は、下記の反応式（Ｉ）に示すように、まず酸無水物とジアミンが反応してポリアミック酸膜が形成された後、ポリアミック酸の脱水閉環反応が進行することによって行われるものである。

【００２３】

【化１５】

11　　12



（Ｉ）

【００２４】ここで式中のR₅、R₆で示される部分は式（Ａ）乃至（Ｆ）で示される酸無水物及びジアミンに対応するように任意に選択されるものであり、ｎは自然数である。このようにして形成される本発明のポリイミド蒸着重合膜は膜厚を均一に形成することができるものであり、また可撓性が高く、ポリイミド蒸着重合膜が形成された基材に機械加工等を行って外力を加えてもひび割れや剥離が生じにくいものであって、電磁材料に使用する基材に適用する際、その電気絶縁性や表面保護性を向上することができるものである。

【００２５】

【実施例】以下、本発明を実施例によって詳述する。

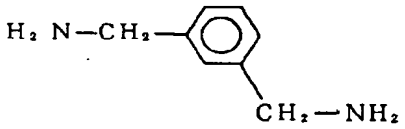
（実施例１乃至９）基材として、電磁軟鉄にプレス加工を施して図２に示すように、幅d_1＝１３ｍｍ、奥行きd_4＝３ｍｍ、厚みd_5＝１ｍｍの基部１３の両端に、高さd_6＝３ｍｍ、厚みd_3＝１ｍｍの片部１４、１４が立設されて片部１４、１４間の寸法がd_2＝１１ｍｍとなった形状の鉄芯１２を形成し、この表面に銅めっき＊及びニッケルめっきを施した。

【００２６】各実施例について、上記の鉄芯１２に表１に示す酸無水物及びジアミンを用いてポリイミド蒸着重合膜を形成した。ポリイミド蒸着重合膜を形成する際は、酸無水物及びジアミンを各２０ｇ用い、酸無水物を２８０℃、ジアミンを２６０℃で蒸発させて蒸着槽へ導入し、蒸着槽内で、反応温度２３０℃、反応圧力2×10^{-2}Ｔｏｒｒの条件で鉄芯１２上に表１に示す膜厚のポリイミド蒸着重合膜を形成した。

【００２７】ここで表１中の酸無水物（Ｇ）、（Ｂ）、（Ｃ）は、それぞれ上記化学式（Ｇ）、（Ｂ）、（Ｃ）で示される酸無水物であり、ジアミン（Ｈ）は上記化学式（Ｈ）で示されるジアミン、ジアミン（Ｊ）、（Ｋ）はそれぞれ下記化学式（Ｊ）、（Ｋ）で示されるジアミンである。

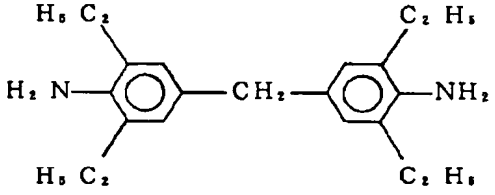
【００２８】

【化１６】



（Ｊ）

【００２９】　※　※【化１７】



（Ｋ）

【００３０】（比較例１）酸無水物として上記化学式（Ｇ）で示される酸無水物を用いると共に、ジアミンとしてＯＤＡ（４，４’－ジアミノジフェニルエーテル）を用いた以外は実施例１と同様に行って、鉄芯１２に膜厚１０μｍのポリイミド蒸着重合膜を形成した。

（初期耐電圧評価）各実施例及び比較例のポリイミド蒸着重合膜を形成した鉄芯１２に、ウレタン被覆を施したφ０．．０４２ｍｍのリード線を２０回巻き回した後、リード線の末端の被覆を剥がすと共に、鉄芯１２のポリイミド蒸着重合膜を一部剥がして金属面を露出させた。このような試料を各実施例及び比較例について３０個づつ用意し、鉄芯１２の金属露出面とリード線の金属露出面にそれぞれプローブを当て、絶縁破壊試験器（菊水電子製、品番「ＴＯＳ８６５０」）にて電圧をスローアップで印加して、リーク電流が１０ｍＡのときに絶縁破壊が生じたものとして評価した。

13

（機械加工後の耐電圧評価）各実施例及び比較例にて形成したポリイミド蒸着重合膜を形成した鉄芯１２を、図３（ａ）に示すように両端を固定治具１６に固定し、鉄芯１２の基部１３の端部付近に成形金型１５を取着すると共にこの成形金型１５にＬＣＰ樹脂を注入、硬化させて図３（ｂ）に示すように基部１２の端部付近にＬＣＰ樹脂成形物から成るつば部１７を形成した。更に図３（ｃ）に示すようにこの鉄芯１２の基部１３のつば部１５に挟まれた部分に、ウレタン被覆を施したφ０．０４２ｍｍのリード線１９を、このリード線１９に４ｇの張力をかけながら巻線機にて１５０００ターン巻き回してコイル１８を形成した。このような試料を各実施例及び比較例について３０個づつ用意し、このコイル１８につ＊

14

＊いて、初期耐電圧評価の場合と同様にして耐電圧を評価した。

（耐サージ電圧評価）各実施例及び比較例の鉄芯１２を用いて、機械加工後の耐電圧評価の際と同様にコイル１８を形成し、このコイル１８を用いてリレーを組み上げた。このような試料を各実施例及び比較例について３０個づつ用意し、このリレーの接点とコイル端子との間にサージ電圧を１．２×５０μｓｅｃ．の標準衝撃電圧波形で、波高値を１５００Ｖから２５０Ｖ毎に上昇させて繰り返し印加し、絶縁破壊が生じる限界値を測定した。

【００３１】以上の結果を表１に示す。

【００３２】

【表１】

			実施例									比較例
			1	2	3	4	5	6	7	8	9	1
蒸着重合膜	酸無水物		(G)	(G)	(G)	(B)	(B)	(B)	(C)	(C)	(C)	(G)
	ジアミン		(H)	(J)	(K)	(H)	(J)	(K)	(H)	(J)	(K)	ODA
	膜厚（μm）		8	8	8	8	8	8	8	8	8	10
評価試験	初期耐電圧（V）	平均値	2210	2110	2140	2240	2170	2180	2040	1980	2140	2000
		最大値	2550	2440	2410	2500	2400	2410	2410	2320	2410	2430
		最小値	1950	1900	1880	1980	1880	1930	1780	1880	1880	1850
	機械加工後の耐電圧（V）	平均値	2250	2150	2190	2220	2180	2190	2010	2090	2190	1750
		最大値	2650	2530	2530	2580	2500	2590	2380	2430	2530	2200
		最小値	1900	1790	1850	1950	1820	1960	1870	1850	1980	1200
	耐サージ電圧（V）	平均値	2130	1980	2070	2110	2020	2070	2000	1940	1930	1900
		最大値	2250	2250	2250	2250	2250	2250	2250	2250	2250	2000
		最小値	2000	1750	2000	2000	1750	2000	1750	1750	1750	1750

【００３３】表１から判るように、比較例１では初期耐電圧と比較して機械加工後の耐電圧が低下し、また耐サージ電圧も実施例１乃至９のものよりも低く、鉄芯１２の固定治具１６への固定、成形金型１５の取着、リード線１９の巻き回し等の機械加工による外力によって、ポリイミド蒸着重合膜のひび割れや剥離が生じ、鉄芯１２の電気的絶縁性が低下したものである。それに対して実施例１乃至９のものでは、初期耐電圧と機械加工後の耐電圧との差はほとんどなく、また耐サージ電圧も比較例１のものよりも高いものであり、本発明のポリイミド蒸着重合膜の高い可撓性により機械加工により外力がかけられた後もポリイミド蒸着重合膜のひび割れや剥離の発生が抑制され、鉄芯１２の電気的絶縁性を維持することができたことが確認できた。

【００３４】

【発明の効果】上記のように本発明のポリイミド蒸着重合膜は、上記化学式（Ａ）乃至（Ｃ）で示される酸無水物のうち少なくとも一つと、上記化学式（Ｄ）乃至（Ｆ）で示されるジアミンのうち少なくとも一つとの蒸着重合にて形成されるため、可撓製が高く、このポリイミド蒸着重合膜を形成した基材に機械加工等を施して外力を加えた際のポリイミド蒸着重合膜のひび割れや剥離の発生を抑制することができ、基材として電磁材料を用いたときの基材の電気的絶縁性を向上することができるものである。

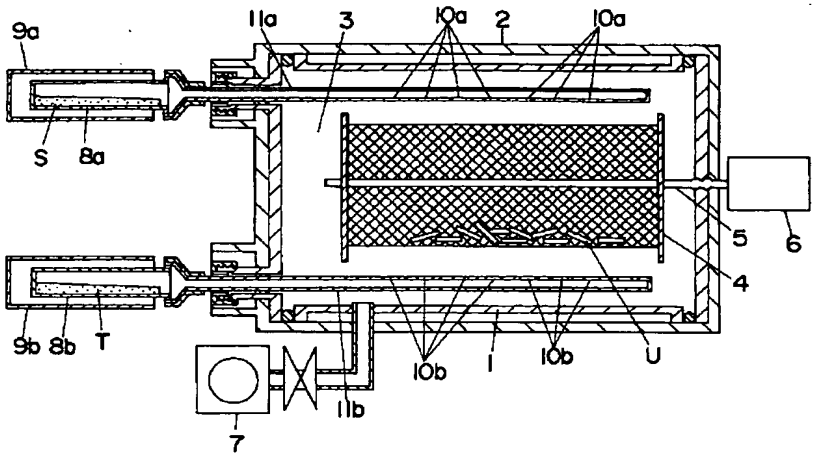
【図面の簡単な説明】

【図１】本発明のポリイミド蒸着重合膜を形成するために用いる蒸着重合装置の一例を示す断面図である。

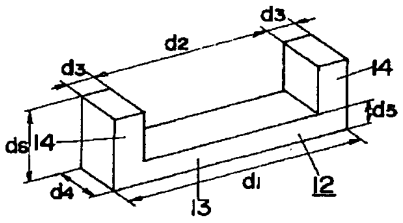
【図２】実施例１乃至９及び比較例１にて用いた鉄芯を示す斜視図である。

【図３】（ａ）乃至（ｃ）は、同上の鉄芯からコイルを形成する各工程を示す正面図である。

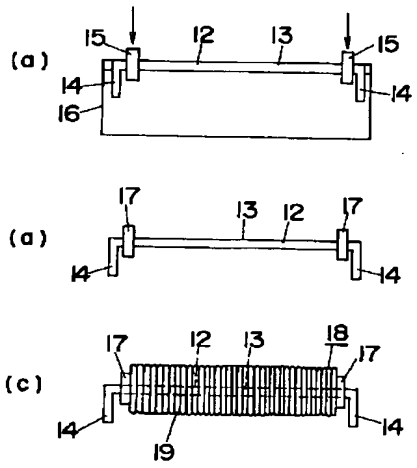
【図１】


9a
11a
3
10a
2
10a
S
8a
5
6
4
9b
8b
T
10b
1
10b
U
11b
7

【図２】


d3
d2
d3
14
d5
d5
14
d4
d1
13
12

【図３】


(a)
15
12
13
15
14
14
16
(a)
17
13
12
17
14
14
(c)
17
12
13
18
17
14
14
19